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1 **Global climate stabilisation by chemical weathering during the Hirnantian**
2 **glaciation**

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21 **Chemical weathering of silicate rocks is a primary drawdown mechanism**
22 **of atmospheric carbon dioxide. The processes that affect weathering are**
23 **therefore central in controlling global climate. A temperature-controlled**
24 **“weathering thermostat” has long been proposed in stabilising long-term**
25 **climate, but without definitive evidence from the geologic record. Here we**

use lithium isotopes ($\delta^7\text{Li}$) to assess the impact of silicate weathering across a significant climate-cooling period, the end-Ordovician Hirnantian glaciation (~445 Ma). We find a positive $\delta^7\text{Li}$ excursion, suggestive of a silicate weathering decline. Using a coupled lithium-carbon model, we show that initiation of the glaciation was likely caused by declining CO_2 degassing, which triggered abrupt global cooling, and much lower weathering rates. This lower CO_2 drawdown during the glaciation allowed climatic recovery and deglaciation. Combined, the data and model provide support from the geological record for the operation of the weathering thermostat.

The recovery and stabilisation of Earth's climate system from perturbations is central to the continued survival of life. Chemical weathering of continental silicate rocks driving marine carbonate precipitation is the Earth's primary long-term mechanism for removal of atmospheric CO_2 (BERNER, 2003). A temperature feedback control on weathering rates (i.e. greater temperatures cause higher weathering rates, removing more CO_2) would result in a climate-stabilising mechanism. This "weathering thermostat" has long been postulated and assumed in models (COLBOURN *et al.*, 2015). However, direct evidence for weathering rate changes in response to climate perturbations has been harder to pin down in the geological record.

The Late Ordovician Hirnantian (~445 Ma) records the second largest mass extinction in Earth history. This was likely caused by rapidly decreasing temperatures, culminating in an ice-sheet over Gondwana (ELRICK *et al.*, 2013). As such, similarities exist between the Hirnantian and the Late Cenozoic

51 glaciations (GHIEPNE *et al.*, 2014). The behaviour of atmospheric CO₂ is of
52 particular interest, because of the potential role of declining CO₂ in initiating the
53 glaciation and of increasing CO₂ in terminating it (VANDENBROUCKE *et al.*, 2010).
54 Either or both could have involved changes in silicate weathering rates (BERNER,
55 2003). The combination of changes in weathering rates and pCO₂ also resulted in
56 a global positive $\delta^{13}\text{C}$ excursion (HICE) (LENTON *et al.*, 2012; GHIEPNE *et al.*, 2014).
57 Osmium isotopes have suggested a decline in weathering during the glacial
58 maximum (FINLAY *et al.*, 2010). However, Os mainly traces weathering
59 provenance, rather than weathering rates or processes. Lithium isotopes are the
60 only tracer available whose behaviour is solely controlled by silicate weathering
61 processes, and therefore give a unique insight into CO₂ drawdown and climate-
62 stabilisation.

63 Lithium isotopes ($\delta^7\text{Li}$) are not fractionated by biological processes
64 (POGGE VON STRANDMANN *et al.*, 2016), and are not affected by carbonate
65 weathering (DELLINGER *et al.*, 2015). The $\delta^7\text{Li}$ of primary silicate rocks defines a
66 narrow range (continental crust $\sim 0.6 \pm 0.6\text{‰}$, basalt $\sim 3\text{--}5\text{‰}$ (SAUZEAT *et al.*,
67 2015)) compared to the high variability in modern rivers ($2\text{--}44\text{‰}$ (HUH *et al.*,
68 1998; DELLINGER *et al.*, 2015; POGGE VON STRANDMANN AND HENDERSON, 2015)).
69 Riverine values reflect weathering processes, particularly the extent of
70 preferential uptake of ^6Li into secondary minerals (DELLINGER *et al.*, 2015), and
71 therefore reflect “weathering congruency”, defined as the ratio of primary rock
72 dissolution (driving rivers to low, rock-like, $\delta^7\text{Li}$ = congruent dissolution of rock),
73 to secondary mineral formation (driving rivers to high $\delta^7\text{Li}$) (MISRA AND FROELICH,
74 2012; POGGE VON STRANDMANN AND HENDERSON, 2015). In modern oceans, rivers
75 ($\sim 50\%$ of the ocean input, with a mean $\delta^7\text{Li} \sim 23\text{‰}$ (HUH *et al.*, 1998)) are

combined with mid-ocean ridge hydrothermal solutions (~50%, with a mean $\delta^7\text{Li}$ ~7‰ (CHAN *et al.*, 1993)). The oceanic sinks are incorporation into low-temperature clays in altered oceanic basalt (AOC) and marine authigenic clays (MAAC), which cumulatively impose isotopic fractionation of ~15‰, driving modern seawater to 31‰. Marine carbonates represent a negligible sink for Li, and their isotopic fractionation factor remains approximately constant at ~3–5‰, independent of temperature, salinity, or whether the calcite is inorganic or skeletal (MARRIOTT *et al.*, 2004; POGGE VON STRANDMANN *et al.*, 2013).

Here we present $\delta^7\text{Li}$ from bulk carbonates and brachiopods from Anticosti Island, Canada (ACHAB *et al.*, 2013) (Pointe Laframboise and Ellis Bay West), and from an equivalent shale section at Dob's Linn, UK (FINLAY *et al.*, 2010; MELCHIN *et al.*, 2013) (see Supplement for methods and data). The $\delta^7\text{Li}$ values from all sections exhibit a positive excursion of ≤ 10 ‰ before the HICE (Fig. 1). We rule out effects on carbonate $\delta^7\text{Li}$ by silicate leaching, due to our processing technique (see Supplement). We also rule out diagenesis, because trends and absolute values of $\delta^7\text{Li}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (MELCHIN *et al.*, 2013) are reproduced in different sections, both bulk carbonates and brachiopods (Fig. 1). Overall, therefore, this suggests that the Li isotopic excursion represents a primary seawater signal.

While carbonates tend to be the usual seawater archive (e.g. (MISRA AND FROELICH, 2012; POGGE VON STRANDMANN *et al.*, 2013), silicates have also been investigated (DELLINGER *et al.*, 2017), and sediments older than Ordovician are considered to represent pre-depositional (unaltered by diagenesis) weathering signals (LI *et al.*, 2016). Hence, detrital clays (which dominate at Dob's Linn) should reflect changing local continental weathering conditions (see Supplement

and Fig. S4). Tracers such as Si/Al, Li/Al or $^{187}\text{Os}/^{188}\text{Os}$ rule out control by changing provenance or clay mineralogy. Dob's Linn exhibits an isotope excursion of similar magnitude, but $\sim 14\text{‰}$ lower than the carbonates. While biostratigraphy suggests that the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ of Anticosti and Dob's Linn are slightly offset (MELCHIN *et al.*, 2013)(Fig. 1), in all sections the relative timings of the $\delta^7\text{Li}$ and HICE are similar. Chemostratigraphy therefore suggests the Li isotope excursions occur contemporaneously (see Supplement), consistent with lithium's long modern ocean residence time (~ 1 Myr). A simple temperature dependence of the clay fractionation factor during weathering would only cause $<1.6\text{‰}$ variation (LI AND WEST, 2014), and is therefore not the cause of the observed variability. Although shales, in particular clay fractionation factors, are under-constrained for a quantitative interpretation in isolation, their comparison to and temporal similarities with carbonates suggests a link. Thus, global seawater compositions (represented by carbonates) appear to be responding to the same driving force as this local archive of continental weathering (represented by shales).

The pre- and post-excursion $\delta^7\text{Li}_{\text{seawater}}$ values of $\sim 15\text{‰}$ are difficult to achieve in a modern ocean. It is likely that the AOC and MAAC sinks were broadly similar to today (HAZEN *et al.*, 2013), imparting an isotopic fractionation factor of $\sim 15\text{‰}$, which may be temperature-dependent, as discussed below. We do not consider a "sink-shift" between proportions of MAAC vs. AOC, as proposed for the Cenozoic (LI AND WEST, 2014), because the Hirnantian duration is likely too short (1–2 Myr) for a transient change. Therefore, Li inputs must have had an isotope ratio close to 0‰ . Assuming a modern-like hydrothermal input, this requires that rivers had $\delta^7\text{Li}$ values essentially unfractionated from the

continental crust (modern value $\sim 0\text{‰}$ (SAUZEAT *et al.*, 2015)). This possibility is supported by $\delta^7\text{Li}$ values of $\sim 2\text{‰}$ for the Amazon river (DELLINGER *et al.*, 2015), and similarly low values during the peak of the Cenomanian-Turonian hyperthermal (POGGE VON STRANDMANN *et al.*, 2013). However, data here imply that Ordovician oceans were isotopically light at steady state. Given that the first non-vascular land plants were only just evolving and colonising the continents in the mid-late Ordovician (with associated organic acid production), it is probable that clay types were different and less abundant (HAZEN *et al.*, 2013). For example, illites, which cause little Li isotope fractionation (MILLOT AND GIRARD, 2007), are thought to dominate prior to terrestriation by plants (HAZEN *et al.*, 2013). If this is a feature of early Earth weathering, then the continental crust's $\delta^7\text{Li}$ would have been mantle-like ($\sim 3\text{‰}$), rather than driven isotopically light by weathering.

Assuming, therefore, that silicate weathering was highly congruent, we have created a dynamic non-steady-state coupled Li and C cycle model (see Supplement). In brief, the model uses Li formulations from previous work (POGGE VON STRANDMANN *et al.*, 2013; LECHLER *et al.*, 2015), with an added temperature dependence on the Li sink with a sensitivity of $-0.15\text{‰}/\text{K}$ (LI AND WEST, 2014), and links the weathering flux to that calculated by the carbon cycle model (based on GEOCARB III). Existing climate models suggest that $p\text{CO}_2$ needed to halve to $\sim 8\text{PAL}$ (present atmospheric level) to trigger the Hirnantian glaciation (POHL *et al.*, 2016). This could be initiated by a decline in degassing (MCKENZIE *et al.*, 2016), an increase in plant cover (LENTON *et al.*, 2012) or uplift (KUMP *et al.*, 1999), or a combination of these. A rather extreme decline in degassing from the initial Ordovician value of $1.55\times$ to $0.75\times$ modern causes CO_2 to drop to $\sim 6.5\text{PAL}$.

Both the hydrothermal and riverine Li fluxes scale proportionally to degassing, resulting in no steady-state change, but a transient adjustment of the oceanic Li reservoir causes a positive $\delta^7\text{Li}$ excursion of $\sim 3.5\text{‰}$ (i.e. correct direction, but smaller excursion). In contrast, increasing plant-induced weathering (and associated clay mineral formation) causes a permanent, rather than transient $\delta^7\text{Li}$ increase (see Supplement), which is not observed in our data. However, it is possible that the two processes operated in conjunction. A 65% increase in uplift would create the same effect, but would be unprecedented in the Phanerozoic. Theoretically, the excursion could also be caused by an increase in riverine $\delta^7\text{Li}$ by $\sim 15\text{‰}$ with no change in flux. However this is unlikely, because it implies greater uptake into clay minerals, which would cause a decrease in river flux. This scenario also has no carbon cycle forcing, and hence we prefer a coupled flux and isotope ratio change, initiated by a degassing change.

A recent insight is that a glacial “tipping point” existed in the Late Ordovician, where, once global temperature dropped to a critical threshold, northern high latitude sea-ice expanded abruptly, causing a further decrease in global temperatures and rapid expansion of an ice sheet on the Southern polar land surfaces (POHL *et al.*, 2016). These ice-albedo and heat transport feedbacks operate far faster than the long-term carbon cycle. Hence to represent this we implement an abrupt cooling when CO_2 reaches $\sim 8\text{PAL}$, generating reduced silicate weathering rates. To prevent an immediate abrupt warming, we assume some bi-stability of temperature and ice cover such that CO_2 has to rise to $>8\text{PAL}$ before deglaciation occurs. The cooling-induced reduction in global weathering flux (by $\sim 4\times$), causes an accelerated rise in $\delta^7\text{Li}$ from 17–19‰ (depending on continental crust composition) to $>25\text{‰}$ (Fig. 2), which is reversed when the

build-up of CO₂ triggers abrupt warming and deglaciation. Hence peak $\delta^7\text{Li}$ is predicted to be at the end of the glacial interval, consistent with sea-level reconstructions (Fig. 2). The size of the excursion could be increased by coupling the weathering decline with higher riverine $\delta^7\text{Li}$, as suggested by the shale record (Fig. 2). This could be caused by an increase in the continental residence time of water allowing more clay formation, or a temperature-dependent shift in clay mineralogy. Such a change in congruency could also assist a vegetation-accelerated scenario, where terrestrialisation enhanced weathering, but enhanced glacial grinding forced a return to more congruent weathering. Such vegetative forcing would also cause a transient $\delta^7\text{Li}$ excursion (Fig. S9), albeit one of longer duration, hence we consider this less likely. Critically, the model can explain an increase in $\delta^7\text{Li}$ as cooling starts, but before the full glaciation was initiated, and the highest oceanic $\delta^7\text{Li}$ occurring at the end of the glaciation as observed in the record. $^{187}\text{Os}/^{188}\text{Os}$ values (FINLAY *et al.*, 2010) agree with this scenario, suggesting inhibition of weathering by cooling (which would also increase CO₂ (KUMP *et al.*, 1999)) and hence a change in provenance focus, coincident with the $\delta^7\text{Li}$ peak. Our model also predicts $^{87}\text{Sr}/^{86}\text{Sr}$ variation within the observed scatter (SHIELDS *et al.*, 2003), lending further credence to our interpretation (see Supplement).

The data and model are therefore consistent with the Hirnantian glaciation being initiated by declining CO₂ degassing, leading to a transient decline in silicate weathering, in turn causing an atmospheric CO₂ increase that ultimately terminated the glaciation. The Hirnantian has been compared to Cenozoic glaciations (GHIEPNE *et al.*, 2014), where both periods are now characterised by increasing $\delta^7\text{Li}$ values (MISRA AND FROELICH, 2012). The positive

$\delta^7\text{Li}$ excursion during the Hirnantian cooling event also compares well to negative $\delta^7\text{Li}$ excursions during warming events (POGGE VON STRANDMANN *et al.*, 2013; LECHLER *et al.*, 2015). Overall, therefore, this study shows that if a tectonic-driven climate control (degassing) can push the climate system out of balance, a temperature-dependent feedback via silicate weathering will eventually stabilise the climate. Such a weathering thermostat has frequently been postulated as a climate regulating process, but has proven remarkably difficult to unambiguously demonstrate in the geological record.

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Author contributions

PPvS wrote the research proposal, carried out the analyses and wrote the manuscript. TML and PPvS conducted the modelling. AD, AJF and DS provided samples, geochemical context and edited the manuscript. MJM assisted in analyses and edited the manuscript.

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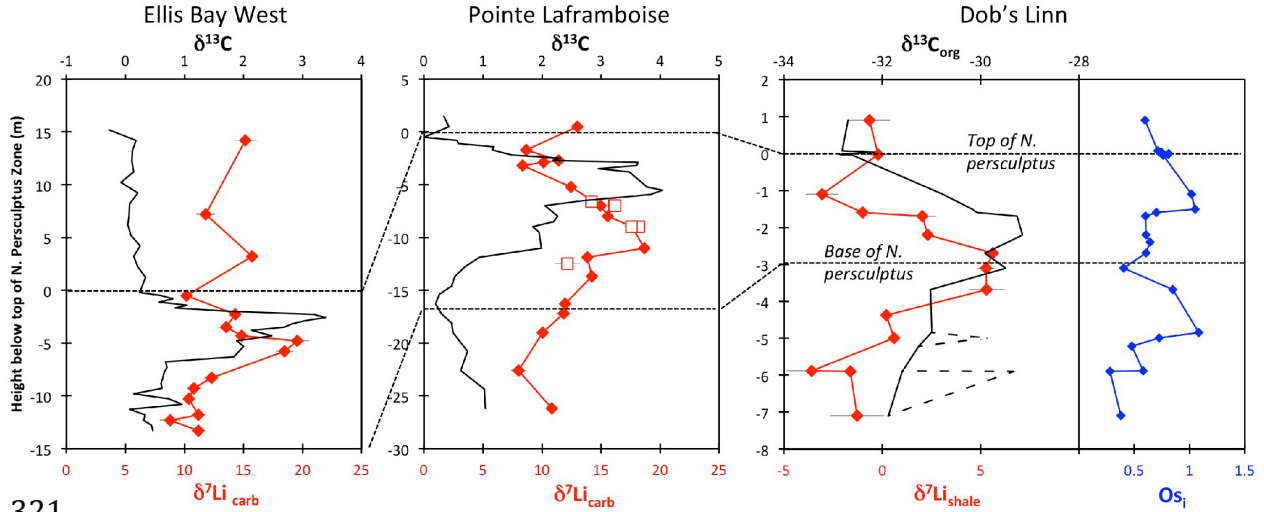


Figure 1. Carbonate (Pointe Laframboise and Ellis Bay West) and shale (Dob's Linn) Li isotope ratios. Open squares are separately analysed brachiopods. Carbon and osmium (initial $^{187}\text{Os}/^{188}\text{Os}$) isotope data are from the same samples (FINLAY *et al.*, 2010). Biostratigraphic correlation is based on the *N. persculptus* zone (MELCHIN *et al.*, 2013).

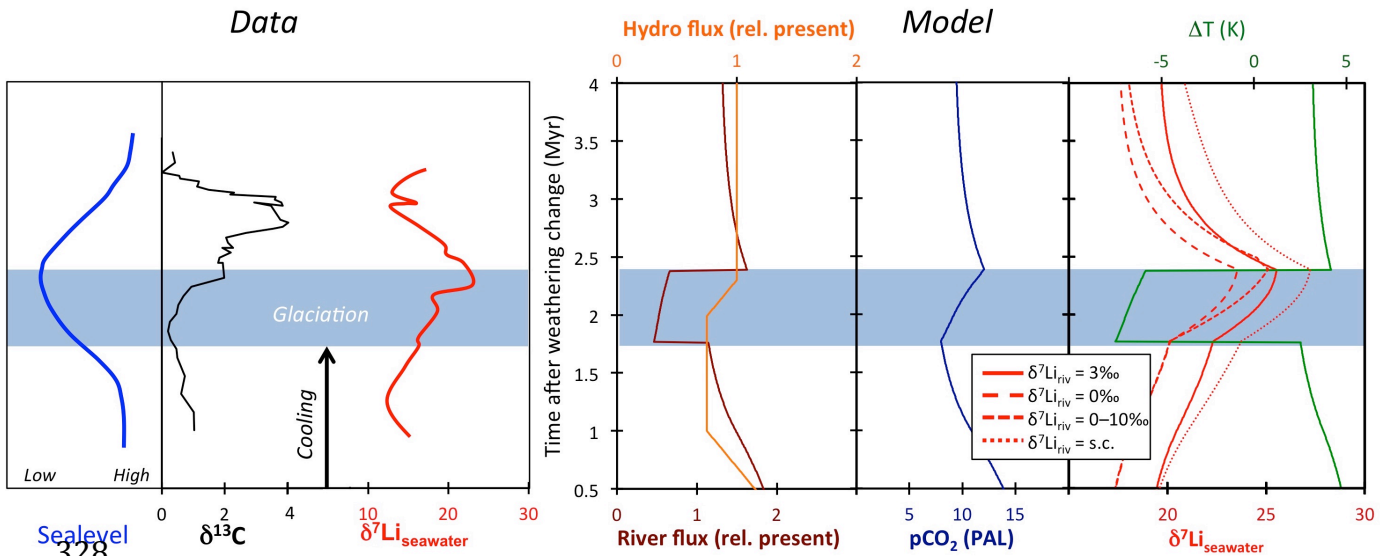


Figure 2. Comparison of data and model results. Sea level timing is from stratigraphic data (GHIENNE *et al.*, 2014). Seawater Li isotope data were generated from carbonate data by adding a 4‰ fractionation factor (MARRIOTT *et*

332 *al.*, 2004). The model shows the changes in riverine and hydrothermal Li fluxes,
333 the pCO₂ levels and temperature anomalies caused by these changes, and the
334 resulting oceanic $\delta^7\text{Li}$ curve. The red model lines are for scenarios where riverine
335 $\delta^7\text{Li} = 3\text{‰}$, 0‰, a change from 0 to 10‰ during the glaciation and “shale-
336 constrained” (s.c.), using Dob’s Linn $\delta^7\text{Li}$ data to constrain river values (see text
337 and supplement for detail).